

# Selectivity of solid-contact Ag potentiometric sensors based on thiacalix[4]arene derivatives

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## ARTICLE INFO

### Article history:

Received 4 September 2007

Received in revised form 17 March 2008

Accepted 21 March 2008

Available online 28 March 2008

### Keywords:

Potentiometric sensor

Thiacalixarene

Host-guest complexation

Silver determination

## ABSTRACT

Potentiometric sensors based on glassy carbon electrode covered with polyaniline containing amidopyridine, morpholide, pyrrolidide and hydrazide functional groups in cone and 1,3-alternate conformations have been developed and applied for Ag<sup>+</sup> determination in the range from  $1.0 \times 10^{-2}$  to  $4.0 \times 10^{-7}$  M and limits of detection from  $1.0 \times 10^{-7}$  to  $4.0 \times 10^{-8}$  M. Sensitivity of Ag<sup>+</sup> detection decreases in the following range of thiacalix[4]arene derivatives: morpholide > pyrrolidide > amidopyridine > hydrazide. Potentiometric selectivity showed binding of Ag<sup>+</sup>, Hg(II) and Fe(III) ions over other transition and alkali metal ions. Stereoelectronic groups and conformation of receptor on the selectivity of the sensor response have been shown, selectivity and sensitivity of Ag<sup>+</sup> determination depends on the stereoelectronic site and flexibility of the receptor structure. For Fe(III) ions, changes of the potential were determined by their implementation in redox reactions of polyaniline.

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## 1. Introduction

The interest to the development of novel potentiometric sensors and their application in biology, medicine, environmental monitoring, industry and agriculture is currently stimulated by the advantages they possess, i.e. low cost, simple operation, flexible production, a wide range of concentrations to be determined, adequate sensitivity and selectivity [1]. Current research activity in this area includes the construction of maintenance-free sensors with high stability of the response and diverse selectivity toward analytes [2,3]. This can be achieved by combination of novel neutral ionophores with conducting polymers which provide ion-to-electron transduction and can be used as a matrix for incorporating the specific receptors or other additives entrapped into the polymer film due to electrostatic interactions.

Polyaniline (PANI) [4–7], polythiophene derivatives [8–11], polypyrrole [7,11–14], polyanisidine [7], polycarbazole [15] were investigated in the assembly of solid-contact potentiometric sensors. For PANI, strong pH-sensitivity of its potential can limit its sensor applications. However, the use of additional polymeric membranes with lipophilic salts and PANI encapsulation as well as introduction of substituents at nitrogen atom of the polymeric

chain partially diminish the pH dependence and can increase its reversibility [16–20].

Among other ionophores, substituted calixarenes and their analogs have been intensively investigated as recognition elements toward inorganic and organic species [21–23]. The calixarene moiety ensures the coordination of the binding sites and hence controls the reactivity and selectivity of the receptor toward organic and inorganic compounds. Thus, calixarenes containing pendant ether, ester, amide and ketone groups. Mono- and bis-calix(crowns) exhibit a selectivity toward alkali-earth metal ions [24–27]. The introduction of nitrogen atoms into the substituents increases the selectivity of the calixarenes with soft transient metal ions. Substituted arylamide [28] and tetrasubstituted calixarenes [29] calix[4]arenes show selective binding compared with parent calixarenes, thiacalixarenes provide opportunities for binding metal ions which do not bridge bridging sulfur atoms [30]. Recently, a number of thiacalixarenes with  $\pi$ -coordinating centers were investigated for potentiometric selectivity for Ag(I) determination. The limit of  $3 \times 10^{-11}$  M was found for bridged thiacalixarenes in potentiometric measurements [31]. Unsubstituted *p-tert*-butylthiacalixarene were deposited onto the gold electrode and active part of the electrode for Cu(II) determination [32–34]. Sulfonated thiacalixarenes were applied for pre-column concentration

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